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SUITABILITY OF POLYVINYL CHLORIDE PIPE FOR MONITORING  
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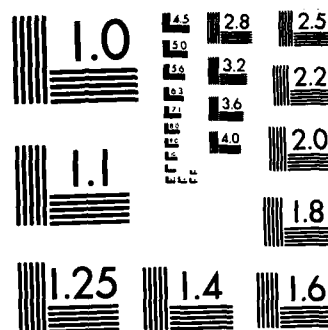
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# Special Report 85-12

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**US Army Corps  
of Engineers**

Cold Regions Research &  
Engineering Laboratory

## *Suitability of polyvinyl chloride pipe for monitoring TNT, RDX, HMX and DNT in groundwater*

L.V. Parker, T.F. Jenkins and B.T. Foley

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## 20. Abstract (cont'd)

pH and dissolved oxygen. The only case where there was increased loss of any substance because of the presence of PVC pipe was in the TNT solution under nonsterile conditions. This increased loss was thought to be associated with increased microbial degradation rather than sorption. Therefore, given the length of time of this experiment and the small amount of loss attributable to sorption, PVC groundwater monitoring pipe is acceptable for monitoring groundwater for these munitions. Several samples of PVC pipe were also leached with groundwater for 80 days and no detectable interferences were found by reversed phase HPLC analysis.

## PREFACE

This report was prepared by L.V. Parker, Physical Scientist, Applied Research Branch, Experimental Engineering Division, T.F. Jenkins, Research Chemist, and B.T. Foley, Physical Science Technician, both of the Earth Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory.

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This report was technically reviewed by M. Stutz, Analytical Branch, Technology Division, USATHAMA; D.C. Leggett of CRREL and Dr. C.L. Grant, Department of Chemistry, University of New Hampshire; the authors thank them for their suggestions and comments.

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# SUITABILITY OF POLYVINYL CHLORIDE PIPE FOR MONITORING TNT, RDX, HMX AND DNT IN GROUNDWATER

by

L.V. Parker, T.F. Jenkins and B.T. Foley

## INTRODUCTION

Polyvinyl chloride (PVC) is commonly used to fabricate groundwater monitoring pipe because of its strength, corrosion resistance, weatherability, weight and cost. However, it has not been determined whether pipe made from this material is acceptable for many groundwater monitoring applications. It may sorb contaminants and thereby lower their concentrations, or it may leach contaminants that interfere with analysis. Specifically, we wanted to determine if PVC groundwater monitoring pipe was acceptable for use in monitoring for the explosives TNT, RDX and HMX, and DNT, which is often found as a contaminant in production grade TNT.

PVC is a polymer with the structure  $(CH_2CHCl)_n$  formed from covalently bonded vinyl chloride monomers  $(CH_2 = CHCl)$ . Commercial grades of PVC have a molecular weight in the 50,000 to 120,000 range (Roff et al. 1971). The resin is compounded so that it will have specific mechanical, physical or electrical properties by the addition of various plasticizers, fillers, colorants, stabilizers, lubricants and impact modifiers (Penton/IPC, Inc. 1980). Plasticizers are added to give PVC flexibility and are used in the manufacture of sheeting, tubing, film and other flexible forms. Fillers normally impart specific mechanical, physical or electrical properties. Colorants can be dyes or pigments. Stabilizers are usually antioxidants, although there are stabilizers that retard thermal and photochemical degradation as well. Lubricants are used in the molding process to help the plastic part come out of its mold.

Specifications for the manufacture of PVC pipe are promulgated by two organizations: the American Society for Testing and Materials (ASTM) and the National Sanitation Foundation (NSF). The NSF has set criteria for the chemical composition of test water that has been in contact with PVC pipe for the following substances: antimony, arsenic, barium, cadmium, chromium, lead, mercury, selenium, tin, phenolic substances and vinyl chloride monomer. These standards are based in part on the U.S. Environmental



Protection Agency's National Interim Primary Drinking Water Regulations (USEPA 1975). According to ASTM (1980) standards, rigid PVC resin used in the manufacture of schedule 40 and 80 pipe must consist of at least 80% vinyl chloride. The specifications state that other compounding ingredients may include lubricants, stabilizers, resin modifiers and pigments essential for processing, property control and coloring.

A number of substances have been found to leach from various types of PVC, and these include: vinyl chloride monomer (VCM), plasticizers (phthalate esters), stabilizers, impurities and transformation products.

Older studies (Banzer 1977, Dressman and McFarren 1978) found that VCM leached from PVC pipe into water and the amount leached was a function of the residual vinyl chloride monomer (RVCM) concentration in the pipe. However, current NSF standards have reduced this problem by setting the maximum limit of RVCM in PVC pipe at 10 ppm (NSF 1980). Analyses indicate that this level of RVCM results in concentrations of VCM of less than 50 ppb in the water passing through PVC pipe.

Some of the earliest reports of plasticizers leaching from PVC involved blood storage bags and haemodialysis tubing (Jaeger and Ruben 1970, 1972; Fayz et al. 1977; Christensen et al. 1976). Jaeger and Ruben (1970) found that proteins (blood and bovine serum albumin) extracted plasticizers from flexible plastic tubing and bags while simple salt solutions did not. Although Junk et al. (1974) reported high levels of plasticizers in water extracts from flexible PVC tubing, we do not expect to find plasticizers leached from rigid PVC pipe since plasticizers are not used in their manufacture (Roff et al. 1971; Penton/IPC, Inc. 1980; ASTM 1980). Barcelona et al. (1984) caution, however, that some manufacturers may include a very low level of plasticizers in the thermal stabilizer component, but the level of the plasticizers would not exceed 0.01% as compared to the 30-50% plasticizer content found in flexible formulations.

Stabilizers have been found to leach from PVC pipe at measurable levels (Boettner et al. 1981, Dietz et al. 1977). The stabilizers used in potable-water pipe, and presumably in monitoring pipe as well, in the U.S. are organometallic salts of tin, calcium, zinc, calcium-zinc and antimony. These stabilizers include methyl-, butyl-, and octyl-tin esters, particularly in lauric, maleic and thioglycolic acids (Boettner et al. 1981). Dietz et al. (1977) found that as the size of the organic moiety increased there was a significant decrease in the amount of tin extracted by water.

Gross et al. (1974) found an effect with pH; they observed a slight increase in the concentration of lead stabilizer leached at pH 5.0 versus pH 7.8. Gross et al. (1974) and Dietz et al. (1977) also found that the amount of leached stabilizer increased as temperature was increased. For example, Dietz et al. (1977) found a substantial increase in methyl-tin and a slight increase in butyl-tin when they were extracted at 50°C versus 25°C. In all these cases, the concentrations of stabilizers leached were less than the limits set by NSF.

Groundwater temperatures are usually less than 25°C, the lower temperature used in the above experiments, and therefore it is unlikely concentrations would even reach these levels.

There is some evidence in the literature that some organic substances are sorbed by PVC. Lawrence and Tosine (1976) found that PVC chips were quite efficient at adsorbing polychlorinated biphenyls (PCBs) from water and wastewater. PCBs are hydrophobic organic chemicals with water solubilities in the micrograms-per-liter range. For example, Aroclor 1254 is a mixture of a number of isomers of PCBs and has a published water solubility of 56 µg/L (Haque et al. 1974). Octanol-water partition coefficients ( $K_{ow}$ ) have been found to correlate with partitioning of organic chemicals between aqueous solutions and the organic matter in soil and sediments (Karickhoff et al. 1979).  $K_{ow}$  may be useful in predicting the partitioning that can occur between aqueous solutions and a PVC surface as well.  $K_{ow}$  values for PCBs are in the  $10^5$  range (Veith et al. 1979), indicating a very strong tendency for these substances to partition into an organic phase.\* While surface energies also play an important role in determining whether an organic substance will adsorb onto another organic substance, it is not surprising, given the  $K_{ow}$  for PCBs, that efficient sorption on PVC was found.

More recently, Miller (1982) tested three types of well casing materials — schedule 40 PVC, polyethylene and polypropylene — for the adsorption of volatile organic pollutants. The organics tested included bromoform, trichlorofluoromethane, trichloroethylene, 1,1,1-trichloroethane, 1,1,2-trichloroethane and tetrachloroethylene. The well casing materials were also tested to determine which samples subsequently leached

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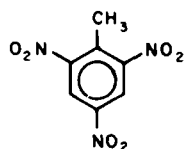
\*The higher the  $K_{ow}$  value, the greater the partitioning will favor octanol and, presumably, an organic surface such as PVC.

the absorbed substance when placed in organic-free water. PVC well casing material was superior to the other two materials and did not adsorb or leach five of the six organics tested. Tetrachloroethylene was sorbed to a slight to moderate extent (25 to 50 percent). It is not certain why tetrachloroethylene was sorbed while the other substances were not. It could be due to its planar geometry, however, which could allow it to more easily penetrate the pores of the polymer. Miller also tested the extent to which these substances leached back into water after PVC had been exposed to low levels of these chemicals. He did not observe any identifiable components from any of the wall casing materials to be tested.

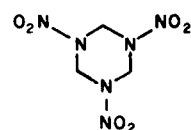
Curran and Tomson (1983) tested five plastics for adsorption of trace levels (0.5 ppb) of naphthalene and *p*-dichlorobenzene. The plastics tested were: Teflon, polyethylene, glued and nonglued rigid PVC, polypropylene and Tygon. Their results are not highly quantitative but they estimate that they recovered 80 to 100% of all of these organics from all of the plastics, with the exception of Tygon. They also tested the plastics for contaminant leaching and found that Teflon showed the least amount of leaching, with rigid nonglued PVC a very close second; Tygon again had the poorest performance. They felt the reason that the leaching values were low for nonglued PVC, when compared to the values of Junk et al. (1974), was because it was rigid and lacked plasticizers.

Barcelona et al. (1985) found a two-fold increase in the sorption of low-molecular-weight halogenated hydrocarbons (chloroform, trichloroethylene, trichloroethane, tetrachloroethylene) with flexible tubings made of PVC, polyethylene, and polypropylene when compared with the sorption found by Miller (1982) for rigid well casings made of the same materials. They hypothesized that sorption of these chlorinated solvents is by absorption into the polymer matrix and that the flexible materials would present a virtual sink for the chlorinated solvent sorbates. They also found 80-90% of the desorption of chloroform occurred almost immediately (within the first 5 minutes).

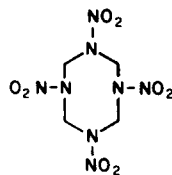
We were unable to locate any specific information in the literature on the interaction of PVC with low concentrations of munitions in aqueous solution. However, data obtained here at CRREL (Leggett, in press) on the filtration of waters contaminated by explosives through PVC membrane filters suggest no adsorptive problems associated with PVC, whereas there were measurable losses with cellulose acetate-nitrate membranes. Broadman



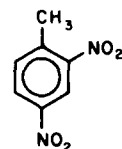
a. TNT.



b. RDX.



c. HMX.



d. DNT.

Figure 1. Chemical structures of four explosives.

et al. (1982) observed hydrogen bonding of 2,4-DNT to nitrocellulose; however, this is unlikely with PVC.

The structural formulas of 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 2,4-dinitrotoluene (DNT) are given in Figure 1.

Table 1 presents a summary of some of their physical properties. DNT is the most water soluble, followed by TNT, RDX and HMX. None of these substances is highly volatile; the highest vapor pressure is  $2 \times 10^{-4}$  torr for DNT.  $K_{OW}$  values for DNT, TNT, RDX and HMX range from 75.2 for DNT to 1.38 for HMX (Table 1). Thus their  $K_{OW}$  values are lower than most of the

Table 1. Physical properties of TNT, DNT, HMX and RDX.

Substance	Melting point °C	Solubility at 24°C (a) (mg/L)	Octanol/water partition coefficient (a)	Vapor pressure at 20°C (torr)	Molecular weight
TNT	80.1(b)	136	45.0	$1.3 \times 10^{-6}$ (d)	227.15
RDX	203.5(c)	43	7.65	$1.0 \times 10^{-9}$ (f)	222.15
HMX	high melting point	5.0(g)	1.38		296.20
DNT	70(b)	180	75.2	$2 \times 10^{-4}$ (e)	182.15

a Leggett (personal communication, 1983, CRREL).

b Dean (1979).

c Hawley (1977).

d Leggett (1977).

e Leggett et al. (1977).

f Coates et al. (1970).

g Glover and Hoffsommer (1973).

organics tested by Miller (1982), Curran and Tomson (1983), and Lawrence and Tosine (1976) against rigid PVC. Therefore, based on previous work with PVC membrane filters and  $K_{ow}$  values, we do not expect significant losses to sorption, but this remains to be verified experimentally.

The objective of this study was to determine if PVC groundwater monitoring pipe is acceptable for use in monitoring groundwater that is contaminated with low levels of military munitions (TNT, RDX, HMX and DNT). Different types of pipe, and pipe from different manufacturers, were tested to determine if there were any differences in the adsorptivity of the pipe. We subsequently investigated whether losses were solely attributable to sorption or whether microbial degradation-biotransformation of the explosives could be involved. We investigated this question under a variety of groundwater conditions by varying the pH, salinity and dissolved oxygen content of the test solution. We also tested two pipes produced by different manufacturers to determine whether any substances that were leached interfered with analyses of these munitions.

#### MATERIALS AND METHODS

##### Materials

Only threaded "monitoring pipe" was used in this study. Threaded pipe was selected to circumvent leaching problems associated with solvent bonded joints. Boettner et al. (1981) have documented that leaching of the solvents used to join PVC pipe can be significant.\* Groundwater monitoring pipe is currently being produced in 2- and 4-in. (5.1- and 10.2-cm) diameters; we tested both. We also tested schedule 40 and 80 pipe. These pipes differ in their strength or wall thickness, i.e., 2-in.-diameter schedule 40 has a wall thickness of 0.154 in. while 2-in.-diameter schedule 80 has a wall thickness of 0.218 in.

##### Analytical methods

We determined TNT, RDX, HMX and DNT using a Perkin Elmer Series 3 High Performance Liquid Chromatograph (HPLC) equipped with a LC-65T variable

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\*Tests we performed with aqueous standards of four common bonding solvents [tetrahydrofuran, cyclohexanone, methylethylketone and methylisobutylketone] indicated, however, that they did not interfere with HPLC analysis of TNT, RDX, HMX or DNT using the mobile phase described above.

wavelength detector set at 254 nm (Jenkins et al. 1984). A 25-cm-long by 4.5-mm-i.d. LC-8 reverse phase HPLC column (Supleco) was used with a mobile phase of 50% water, 38% methanol and 12% acetonitrile (v/v/v). The flow rate was 1.5 mL/min and 100  $\mu$ L of sample was injected using a Rheodyne loop injector operated in the complete fill mode. Under these conditions retention times were: 3.4 minutes for HMX, 4.4 minutes for RDX, 7.5 minutes for TNT and 8.4 minutes for DNT. Peak areas were determined using a Hewlett Packard 3390A Integrator. Detector response was linear with concentration over the experimental range for all four substances.

We prepared analytical standards for TNT, RDX, HMX and DNT by dissolving weighed quantities of SARM\* quality material for each substance in separate 100-mL volumetric flasks with HPLC grade methanol (Baker). From each stock solution 0.500 mL was added to a 1-L volumetric flask and brought to volume with 50:50 methanol/water (Baker HPLC grade methanol and water). The resulting standard contained 614  $\mu$ g/L HMX, 488  $\mu$ g/L RDX, 226  $\mu$ g/L TNT and 271  $\mu$ g/L DNT.

Dissolved oxygen (DO) was determined using the membrane electrode method (APHA-AWWA-WPCF 1980) on a Markson Selectro Mark Analyzer with an Orion O<sub>2</sub> electrode. We determined pH on an Orion 811 pH meter calibrated at pH 4.0 and 7.0 (APHA-AWWA-WPCF 1980). Conductivity was determined using a resistivity bridge according to the method given by APHA-AWWA-WPCF (1980) using 0.1 M, 0.005 M, and 0.001 M KCl standards.

#### Experimental methods

Sections of pipe 4 in. long were placed in 1000-mL glass beakers containing 750 mL of the test solution which had microgram-per-litre levels of TNT, RDX, HMX and DNT. Similar glass controls contained the same amount of sample without any pipe. All samples were covered with a glass to prevent evaporative loss. Solutions used in these experiments were prepared by dissolving known amounts of TNT, RDX, HMX and DNT in local well water from a deep groundwater aquifer. Groundwater was used so that the experiments would be as realistic as possible. This particular source of groundwater had been found in previous work to be very low in organic contaminants that might interfere with analyses. Appendix Table A1 gives some of

\*Standard Analytical Reference Materials supplied by the U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD, 21010.

the physical and chemical characteristics of this water. All experiments were performed at 10°C, a typical groundwater temperature in the U.S., in the dark to prevent any photodegradation.

We did three sets of experiments. In experiment I, we tried to determine if there was any difference in the adsorptivity of different kinds of PVC pipe. We tested for differences in adsorption using duplicate samples of 2-in.-diameter schedule 40 and 80 pipe, 2-in.-diameter schedule 40 slotted well screen, 4-in.-diameter schedule 80 pipe, all manufactured by Timco,\* and 2-in.-diameter schedule 40 pipe manufactured by Eslon Thermoplastics Inc.\*\* The 4-in. sample sections of the 2-in.-diameter pipe were placed in 1000-mL glass beakers containing 750 mL of sample solution and the 4-in. sample sections of the 4-in.-diameter pipe were placed in 2000-mL beakers containing 1500 mL of sample solution. This gave an equal surface-area-to-sample-volume ratio for all the pipe samples. Glass beakers that contained no pipe served as controls. Samples were analyzed on days 0, 14 and 80 and duplicate analyses were performed on each sample.

Experiment II tested whether biodegradation or the presence of PVC pipe, or both, affected the sorption of the four test munitions under a variety of groundwater conditions by varying the pH, dissolved oxygen content (DO) and salinity. Therefore, we tested the effect of sterility, presence of PVC, pH, DO, and salinity on sorption by using a complete 2<sup>5</sup> factorial design. Since we found that autoclaving totally destroyed HMX and RDX in solution, we added HgCl<sub>2</sub> (40 mg/L) to those portions of the solutions used to study the effect of sterility (USGS 1977). We adjusted the pH of the sample solution to an approximate initial value of either 6 with 1.0 M HCl or 8 with 0.1 M NaOH. In those samples where we modified the salinity we added 3.5 µL of a salt solution (50 g/L MgCl<sub>2</sub> + 50 g/L CaCl<sub>2</sub>) per mL of sample solution. To lower the DO content, samples were purged with N<sub>2</sub> gas for several minutes and were then placed in a glove box that was flushed several times with N<sub>2</sub> gas and purged with N<sub>2</sub> at a low rate for the duration of the experiment. The high DO samples were incubated in the presence of air. Schedule 40 2-in.-diameter pipe from Timco Manufacturing Co. Inc. was used throughout. Samples were analyzed on days 0 and 25.

\* P.O. Box 35, Prairie Du Sac, Wisconsin 53578.

\*\* Dept. AV, P.O. Box 240696, Charlotte, N.C. 29224.

Only single analyses were performed because of the large number of samples to be analyzed.

In experiment III we tested Timco and Eslon brands of 2-in.-diameter schedule 40 pipe against glass controls to determine if any substances were leached that interfered with HPLC analyses of the explosives. Duplicate samples of each type of pipe were tested in 1000-mL beakers containing 750 mL of well water that was incubated in the manner described previously. The solutions were analyzed on days 0, 14 and 80.

## RESULTS AND DISCUSSION

### Experiment I

In the first experiment we tested different schedules and diameters of pipe and well screen, and pipe made by different manufacturers. Table 2 shows the results of 14 and 80 days of incubation for different types of PVC pipe with the test solution. It appears there was very little loss of RDX, HMX and DNT even after 80 days, but a fairly large loss of TNT.

After 14 days, the loss of TNT in the PVC samples ranged from 2.9 to 7.2% with 5.4% in the glass control (Table 2). After 80 days there appeared to be more loss in all of the PVC samples than in the glass control. The control samples had a mean concentration of 511  $\mu\text{g/L}$  (18.1% loss). The mean concentration of the pipe samples ranged from 464  $\mu\text{g/L}$  (25.6% loss) for the Eslon 2-in. schedule 40 pipe, to 398  $\mu\text{g/L}$  (36.4%) for the Timco 2-in. schedule 40 pipe. Analysis of variance indicates that the differences in concentration between samples is significant after 80 days of contact (Table A2). We did a least-significant difference test (Steel and Torrie 1960) to determine which samples were significantly different from the others and from the glass control (Table A3). This test indicates that all samples but the one with the Eslon 2-in. schedule 40 pipe had significantly lower TNT concentrations than the glass control. None of the pipe samples that were significantly lower than the glass control were significantly different from each other. Thus while losses of TNT in the presence of PVC were significant when compared with glass, we observed very little variation attributable to differences in schedule, diameter or manufacturer. However, from these data, we cannot be certain to what extent the losses are attributable to sorption or to biodegradation.

There was virtually no change in the concentration of RDX after 80 days in any samples when they were compared with the glass control, except



for the sample containing the Eslon 2-in. schedule 40 pipe, which was considerably higher than the control (Table 2). Analysis of variance indicates there was a highly significant difference between types of pipe (Table A2). However, least significant difference calculations (Table A3) show that this was attributable to the unusually high value in the sample containing the Eslon pipe. All the other types of pipe were not significantly different from the control sample and one another.

Based on the initial concentration of HMX (305  $\mu\text{g/L}$ ) there was very little loss of HMX after 80 days, except from the samples containing the

Table 2. Results from experiment I to test differences in sorption on different types of pipe (concentration in  $\mu\text{g/L}$ ).

Sample	Day 0*	Day 14†	$\bar{x}$ Day 14	Day 80**	$\bar{x}$ Day 80
TNT					
Glass control	624 $\pm$ 25	595 585	590	498;501 522;522	511
Eslon 2-in. sch 40		608 600	604	461;460 467;466	464
Timco 2-in. sch 40		570 602	586	425;417 377;372	398
Timco 2-in. sch 40 well screen		588 572	580	468;425 377;377	412
Timco 2-in. sch 80		580 578	579	455;434 440;434	441
Timco 4-in. sch 80		604 <u>608</u>	606	405;431 <u>419;453</u>	427
		$\bar{x} = 591$		$\bar{x} = 442$	
RDX					
Glass control	1977 $\pm$ 22	2028 2022	2025	2001;2033 2006;2005	2011
Eslon 2-in. sch 40		2069 2040	2054	2061;2058 2069;2059	2062
Timco 2-in. sch 40		2042 2086	2064	2027;1995 2014;1981	2004
Timco 2-in. sch 40 well screen		2051 2033	2042	1979;2005 2008;2028	2005
Timco 2-in. sch 80		2026 2050	2038	2014;2008 1991;1998	2003
Timco 4-in. sch 80		2006 <u>2086</u>	2046	2013;2048 <u>2011;2032</u>	2026
		$\bar{x} = 2045$		$\bar{x} = 2018$	

Table 2 (cont'd).

Sample	Day 0*	Day 14†	$\bar{x}$ Day 14	Day 80**	$\bar{x}$ Day 80
HMX					
Glass control	305±28	290 310	300	318;323 381;362	346
Eslon 2-in. sch 40		281 321	301	335;356 321;329	335
Timco 2-in. sch 40		275 ---	275	313;296 318;310	309
Timco 2-in. sch 40 well screen		303 284	294	284;279 308;283	288
Timco 2-in. sch 80		313 289	301	363;364 309;357	348
Timco 4-in. sch 80		307 <u>267</u>	287	238;269 <u>228;292</u>	257
		$\bar{x} = 295$		$\bar{x} = 314$	
DNT					
Glass control	611±29	612 615	614	620;625 599;602	612
Eslon 2-in. sch 40		--- 618	618	635;615 609;612	618
Timco 2-in. sch 40		605 605	605	610;628 601;608	612
Timco 2-in. sch 40 well screen		607 621	614	654;569 631;599	613
Timco 2-in. sch 80		592 621	607	616;589 606;611	606
Timco 4-in. sch 80		610 <u>624</u>	617	604;605 <u>590;599</u>	600
		$\bar{x} = 613$		$\bar{x} = 610$	

\*This value represents the analysis of the initial sample solution that was used throughout and is the mean of four analyses.

†The two values represent analyses of two separate samples.

\*\*Values on the same line are duplicate analyses of the same sample. Values on the second line represent analyses of a second sample.

Timco 4-in. schedule 80 pipe ( $\bar{x}$  = 257  $\mu\text{g/L}$ ) and to a lesser extent the samples containing the Timco 2-in. schedule 40 well screen ( $\bar{x}$  = 288  $\mu\text{g/L}$ ) (Table 2). However, several samples had higher concentrations on day 80 than they did initially. This discrepancy may be attributable to an analytical problem. We can eliminate the possibility of an interfering substance leaching from the pipe because the concentration in the glass control was also high. Analysis of variance for the day-80 data indicates that there were significant differences between the samples (Table A2). Least significant difference calculations (Table A3) indicate that two of the pipe samples were not significantly different from the glass control (Timco 2-in. schedule 80 pipe and Eslon 2-in. schedule 40 pipe). The least significant difference test also shows that each of the remaining three samples are similar only to their neighbors, based on concentration.

The concentration of DNT appears to have remained constant throughout the entire experiment for all types of pipe and the control (Table 2). The mean concentrations of DNT after 80 days range from 606 to 618  $\mu\text{g/L}$ . As expected, the analysis of variance indicates that there are no significant differences between the different types of pipe and the control sample for DNT (Table A2).

Therefore, while some of the pipe samples did differ from one another in the amount of HMX and TNT lost, we cannot differentiate whether these relatively small losses are due to sorption, biodegradation, or both. In the next experiment we attempt to resolve this question.

## Experiment II

Experiment II utilized a full factorial design to test the effect of sterility, salinity, pH, DO and PVC presence on the loss of TNT, DNT, HMX and RDX from solution. The analyses of the sample solution on day 0 are presented in Table 3. The mean concentrations of TNT, DNT, HMX and RDX initially were 637  $\mu\text{g/L}$ , 544  $\mu\text{g/L}$ , 252  $\mu\text{g/L}$  and 2081  $\mu\text{g/L}$  respectively.

Analyses of the samples after 25 days of incubation at 10°C are given in Table 4. The mean concentration of TNT was 519  $\mu\text{g/L}$  representing an 18.5% loss. This loss appears to be slightly less for the glass control samples ( $\bar{x}$  = 532  $\mu\text{g/L}$  or 16.5% loss) versus the PVC samples ( $\bar{x}$  = 507  $\mu\text{g/L}$  or 20.4% loss). We did a paired t-test to determine if this difference was statistically significant and found that it was significant at the 0.050 level. We then performed an analysis of variance on the data to determine

Table 3. Analysis of sample solutions on day 0 in experiment II (these are the results of single analyses).

Sample*	Concentration ( $\mu\text{g/L}$ )				pH	Conductivity ( $\mu\text{mhos/cm}$ )
	TNT	RDX	HMX	DNT		
1 2 3 4 5						
NS 0 6 - glass	631	2058	285	531	6.5	423
NS 0 6 + glass	636	2073	238	541	7.1	---
NS 0 8 + glass	652	2091	230	538	8.0	1,181
NS 0 8 - glass	632	2089	247	556	8.1	---
S 0 8 + glass	636	2092	262	554	7.8	---
$\bar{x} \pm \text{S.D.}$	637 $\pm$ 9	2081 $\pm$ 15	252 $\pm$ 22	544 $\pm$ 11		

\* Codes for samples by their column number:

- 1) S = sterile - samples incubated with bactericidal agent.  
NS = nonsterile - no bactericidal agent added.
- 2) 0 = samples incubated in normal atmosphere in presence of  $\text{O}_2$ .
- 3) 6 = pH 6, HCL added to lower initial pH to approximately 6.  
8 = pH 8, NaOH added to raise initial pH to approximately 8.
- 4) - = no salts added.  
+ =  $\text{MgCl}_2$  +  $\text{CaCl}_2$  salt solution added.
- 5) glass only or PVC.

all of the significant factors and two-way interactions. Because we did not have any analytical replicates, we grouped all the three-, four- and five-way interactions to form the error term. While the analysis of variance (Table A4) again indicated that PVC-glass interaction (G) was significant at the 0.025 level, it also indicated the interaction of glass and sterility (DG) was significant at the 0.050 level. This means that the loss of TNT from the control samples and from the PVC samples will differ depending upon whether a biocide has been added and that the effect will not be the same in the PVC samples as it is in the control (glass) samples. The mean concentrations were: 529  $\mu\text{g/L}$  in the sterile glass samples, 527  $\mu\text{g/L}$  in the sterile PVC samples, 535  $\mu\text{g/L}$  in the nonsterile glass samples and 489  $\mu\text{g/L}$  in the nonsterile PVC samples.

Table 4. Analysis of sample solutions on day 25 in experiment II (these are the results of single analyses).

Sample*					Sample concentration (µg/L)				DO	pH**	Conductivity
					TNT	RDX	HMX	DNT	(mg/L)		(µmhos/cm)
1	2	3	4	5							
NS	O	6	-	Glass	541	1969	259	510	10.2	8.1	443
NS	O	6	+	Glass	551	1975	244	536	9.8	6.9	1267
NS	O	8	-	Glass	557	1976	262	514	10.3	8.2	380
NS	O	8	+	Glass	516	2000	274	515	10.2	8.1	1266
S	O	6	-	Glass	575	1975	243	529	10.3	7.9	468
S	O	6	+	Glass	589	1972	232	520	9.7	6.8	1268
S	O	8	-	Glass	530	1985	239	578	10.4	8.2	441
S	O	8	+	Glass	546	1995	234	523	10.2	8.2	1266
NS	N	6	-	Glass	532	1959	270	488	1.6	8.6	435
NS	N	6	+	Glass	519	1932	253	470	1.6	8.4	1221
NS	N	8	-	Glass	576	1972	238	534	1.5	8.4	326
NS	N	8	+	Glass	488	1872	280	471	1.4	8.0	1169
S	N	6	-	Glass	527	1905	243	515	1.6	8.2	454
S	N	6	+	Glass	551	1938	242	519	1.9	8.2	1221
S	N	8	-	Glass	419	1919	270	523	1.6	8.7	419
S	N	8	+	Glass	495	1904	247	507	1.5	8.5	1205
NS	O	6	-	PVC	436	1934	261	482	10.4	8.0	394
NS	O	6	+	PVC	515	1992	258	472	9.6	6.9	1266
NS	O	8	-	PVC	509	2005	260	486	10.4	8.1	348
NS	O	8	+	PVC	502	1989	265	592	9.5	7.9	1250
S	O	6	-	PVC	592	1891	221	505	10.9	7.8	479
S	O	6	+	PVC	570	1921	253	487	10.0	6.7	1270
S	O	8	-	PVC	518	1935	281	506	10.6	8.2	432
S	O	8	+	PVC	552	1998	245	527	10.1	7.8	1250
NS	N	6	-	PVC	462	1844	274	481	1.8	8.4	443
NS	N	6	+	PVC	494	2016	264	479	1.6	8.0	1264
NS	N	8	-	PVC	499	1935	260	492	11.4	8.2	306
NS	N	8	+	PVC	492	1949	216	502	1.2	8.1	1198
S	N	6	-	PVC	526	1881	243	556	1.6	8.3	467
S	N	6	+	PVC	544	1879	252	494	1.6	8.2	755
S	N	8	-	PVC	462	1884	284	526	1.5	8.6	412
S	N	8	+	PVC	451	1833	246	502	1.3	8.4	1187
$\bar{X}$					519	1942	253	511			
Shredded											
NS	O	7	-	PVC	536	1988	231	480	10.1	8.1	421

\* Codes for samples by their column number:

- 1) S = sterile = samples incubated with bactericidal agent.  
NS = nonsterile - no bactericidal agent added.
  - 2) O = samples incubated in normal atmosphere, in presence of  $\text{O}_2$ .  
N = samples incubated in glove box flushed with  $\text{N}_2$  gas.
  - 3) 6 = pH 6, HCL added to lower pH to approximately 6.  
7 = nothing added to change pH.  
8 = pH 8, NaOH added to raise pH to approximately 8.
  - 4) - = no salts added.  
+ =  $\text{MgCl}_2$  +  $\text{CaCl}_2$  salt solution added.
  - 5) glass only or PVC.
- \*\* pH obtained on day 25.

The loss of TNT is the same for the sterile glass and PVC samples. Thus it is only when biodegradation can occur that there is an increased loss of TNT in the PVC samples. This increased loss may be attributable to the activity of microorganisms initially present on the PVC pipe, an increased surface area made available by the addition of the pipe for colonization by microorganisms, or a stronger affinity of microorganisms for adhesion to a plastic surface instead of a glass surface,\* or it may be that the pipe leaches some nutrient or growth factor (such as metals) that increases the growth rate or rate of biodegradation. However, we do not attribute this loss to sorption by the pipe because the losses found for the sterile glass samples and the sterile PVC samples were equivalent.

The analysis of variance also indicated several other significant factors and interactions for TNT (Table A4). For example, pH (P) and the interaction of pH and sterility (PD) were significant (0.025 level) and highly significant (0.001 level) respectively. The mean value for the nonsterile pH 8 samples was 517 µg/L, 506 µg/L for the nonsterile pH 6 samples, 497 µg/L for the sterile pH 8 samples and 560 µg/L for the sterile pH 6 samples. We would expect the sterile samples to have a higher concentration than the nonsterile samples since losses from biodegradation have been eliminated. Additional losses observed in the sterile samples at the higher pH may be due to alkaline hydrolysis. Hoffsommer and Rosen (1973) report that TNT is hydrolyzed by alkali. However, they did not observe any hydrolysis of TNT in seawater.

The interaction of DO and sterility (OD) was also significant for TNT. Here we observed increased losses in the nonsterile samples and also in the anaerobic sterile sample. The mean concentration for the sterile aerobic samples was 559 µg/L, 497 µg/L for the sterile anaerobic samples, 516 µg/L for the nonsterile aerobic samples, and 500 µg/L for the nonsterile anaerobic samples. In the nonsterile samples the losses can be attributed to microbial degradation since TNT can be degraded anaerobically as well as aerobically. It is possible that the increased losses in the sterile anaerobic samples are from chemical reduction by cations such as the ferrous ions ( $\text{Fe}^{2+}$ ) initially present in this well water.

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\*Current literature does not agree whether bacteria would adhere more strongly to plastic or glass surfaces (Dahlback et al. 1981).

We also tested the data for significant effects and interactions using the Cuthbert Daniel plotting technique (Daniel 1959). We did this because to do the analysis of variance we had to lump all the three-, four- and five-way interactions to form the error term. While this is common practice, it suffers from a lack of sensitivity because of the possible presence of large higher order interactions. The Cuthbert Daniel test offers the advantage of graphically separating real effects from random error. When we plotted the effects and interactions on the Cuthbert Daniel plot (Fig. A1a) we see that the significance of the previously significant terms (by ANOVA) becomes marginal since they lie close to the 95% confidence level line. This result is consistent with Daniel's (1959) observation that the ability of this technique to discriminate significant effects is reduced when there are a large number of relatively small but significant effects.

Therefore, the statistical analyses indicated there is no significant loss of TNT in the sterile samples that can be attributed solely to the presence of PVC and the increased loss we observed in the nonsterile PVC samples is not from sorption by the pipe but apparently from increased microbial degradation.

RDX showed a mean loss of 6.7% over the 25-day study; as in the first experiment this was considerably less than for TNT. The mean initial concentration was 2081  $\mu\text{g/L}$  and the mean final concentration was 1942  $\mu\text{g/L}$ . Numerically the loss is slightly less in the glass controls ( $\bar{x} = 1953$   $\mu\text{g/L}$  or 6.1% less) than in the samples with PVC pipe ( $\bar{x} = 1930$   $\mu\text{g/L}$  or 7.3% loss). We did a paired t-test to determine if this difference was significant at the 95% confidence level and found it was not. The analysis of variance (Table A4) also indicated that there was no significant difference between the control and PVC samples (G). These results are similar to what we discovered in the first experiment. However, the terms sterility (D) and DO (O) were significant (at the 0.025 level and 0.001 level respectively). The mean concentration of RDX under aerobic conditions was 1969  $\mu\text{g/L}$  compared to 1916  $\mu\text{g/L}$  under anaerobic conditions. The reason that the DO level was highly significant for RDX but not for TNT may be because RDX is subject to biodegradation only under anaerobic conditions (McCormick et al. 1981) while TNT is biotransformed aerobically and anaerobically. (DNT is also subject to degradation aerobically and anaerobically.) The concentration of RDX was also significantly lower in the sterile samples (aerobic

as well as anaerobic) where  $\text{HgCl}_2$  was added. It is possible that this increased loss may be caused by a chemical reaction between RDX and  $\text{Hg}^{2+}$  or an increase in the rate of hydrolysis catalyzed in some fashion by the presence of  $\text{HgCl}_2$ . When we used a Cuthbert Daniel technique to analyze these effects, we found that only oxygen was statistically significant at the 0.050 level (Fig. Alb).

There was no loss of HMX over the 25-day incubation, even under non-sterile conditions. The mean initial concentration was 252  $\mu\text{g/L}$  and the mean final concentration was 253  $\mu\text{g/L}$ . According to McCormick et al. (1981) the rate of biotransformation of HMX is slower than that for RDX and TNT, which may explain in part why we didn't see any losses. The results of the paired t-test indicate that there was no statistically significant difference between the glass controls ( $\bar{x} = 252 \mu\text{g/L}$ ) and the samples with PVC pipe ( $\bar{x} = 255 \mu\text{g/L}$ ). We did see some differences between PVC samples and the control in the first experiment but the test period was a much longer period. Analysis of variance (Table A4), and the Cuthbert Daniel plot (Fig. Alc) indicate that none of the main factors, including glass versus PVC, or their interactions were significant.

The loss of DNT from day 0 ( $\bar{x} = 544 \mu\text{g/L}$ ) to day 25 ( $\bar{x} = 511 \mu\text{g/L}$ ) is relatively low, 6.1%. The loss in the PVC samples ( $\bar{x} = 505 \mu\text{g/L}$  or 7.2% loss) is only slightly greater than that in the glass control samples ( $\bar{x} = 516 \mu\text{g/L}$  or 5.2% loss). Both a paired t-test and an analysis of variance (Table A3) show that this difference was not significant, and that none of the effects or two-way interactions were significant. A Cuthbert Daniel plot of the effects for DNT (Fig. Ald) also indicates that there are no significant factors or interactions.

We ran one other sample during this experiment that contained a large amount of finely shredded PVC pipe. This sample had a large amount of surface area for possible sorption or leaching of reactive compounds (as in the study of Lawrence and Tosine [1976] for PCBs). We did not add any biocide, salt, acid or base and we maintained the sample aerobically. The results of analysis of this sample are given at the bottom of Table 4. The concentrations of TNT, RDX, HMX and DNT were within the range found for the other samples. Thus, even with a large increase in surface area, sorption



did not affect the concentration of these four substances. These results agree with previous work done with PVC membranes by Leggett and Mueller.\*

### Experiment III

In experiment III we tested 2-in. schedule 40 pipe manufactured by Eslon and Timco to see if any substances were leached from the pipe into the well water that interfered with our method of reversed phase HPLC analysis of these explosives. It was possible that the unusually high RDX value for the Eslon pipe seen in experiment II was caused by some substance leaching from the pipe that interfered with RDX analyses. However, even after 80 days we did not detect any spurious peaks from any of the samples using the HPLC method described earlier. While we did not detect any substance being leached from either brand of pipe, this does not necessarily mean that there weren't any compounds leached. There may have been substances that leached that did not interfere with our analyses such as stabilizers. Boettner et al. (1981) found that most of the commercial stabilizers being used to make PVC pipe showed only minor absorption at the wavelength we used, 254 nm.

### CONCLUSIONS AND IMPLICATIONS FOR USE OF PVC PIPE

A study conducted for 80 days under nonsterile conditions to determine the effect of PVC monitoring pipe on aqueous solutions of low levels of TNT, RDX, HMX and DNT indicated that there was a statistically significant loss of TNT and to a lesser extent HMX in the presence of PVC pipe. A follow up study under both sterile and nonsterile conditions indicated that for TNT, this loss is not attributable to adsorption, but seems to be associated with increased microbial degradation. For the most part, the losses of these munitions were equivalent regardless of manufacturer, schedule or diameter of pipe. Well screens showed similar trends.

Long-term leaching studies of PVC monitoring pipe from two different manufacturers indicated that nothing was leached at sufficient concentrations to interfere with reversed phase HPLC analysis of TNT, RDX, HMX or DNT.

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\* Personal communication, CRREL, 1983.

The USATHAMA QA/QC Plan (Sampling and Chemical Analysis Quality Assurance Program for the U.S. Army Toxic and Hazardous Materials Agency) requires contractors to collect samples from groundwater monitoring wells by first purging the well of five times the standing volume of water in the pipe; in wells that are refilling very slowly at least two standing volumes must be purged. The plan specifies that sampling must be conducted immediately after purging is complete, which means that the water sampled will generally be in contact with the well screen and pipe for only a few hours or at most a few days. Based on the results in this study, if low levels of TNT, RDX, HMX or DNT are present in the water, it is very unlikely that interaction with PVC pipe or well screen will significantly modify the concentration of the analyte or leach a substance that will interfere with analysis.

Although we did not test for desorption of these contaminants, leaching studies performed by Curran and Tomson (1983) and Miller (1982) with other organic substances and rigid PVC indicate that if a well were to stand for an extended period of time and was subsequently purged in the manner previously described, we would not anticipate that there would be a significant problem with the leaching of adsorbed contaminants.

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# APPENDIX A: DATA AND STATISTICAL ANALYSES OF DATA SETS

Table A1. Physical and chemical characteristics of well water. pH, total suspended solids, total dissolved solids and specific conductance were determined by methods in APHA-AWWA-WPCF (1980).\* Na, Ca and Mg were analyzed by Furnace AA using Perkin Elmer Model 703AA and HGA-2200 graphite furnace. The Na, Mg and Ca analyses were performed on a different sample.\*\* Total organic carbon (TOC) was determined on an OIC Organic Carbon Analyzer using the persulfate oxidation (ampule) method.\*

pH = 7.3  
 Total suspended solids = <0.1 mg/L  
 Specific conductance = 331  $\mu$ mhos  
 Na<sup>+</sup> = 94 mg/L  
 Mg<sup>++</sup> = 13 mg/L  
 Ca<sup>++</sup> = 167 mg/L  
 TOC = 0.7 mg/L

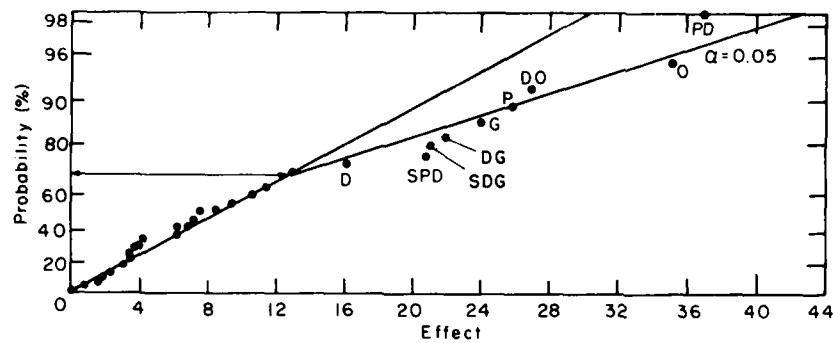
\*Data provided by P. Butler of CRREL.

\*\*Data provided by J. Cragin of CRREL.

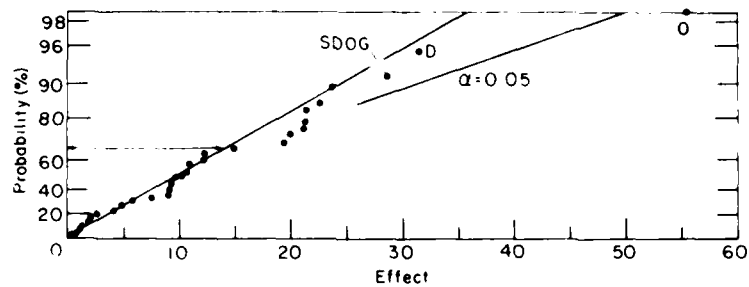
Table A2. Analysis of variance of data from experiment I, day 80.

Term	DF	Mean square	F	Level of significance
TNT				
P	5	3335.8	5.09	0.050
Within cell error	6	655.3		
RDX				
P	5	2090.2	8.55	0.001*
Within cell error	18	244.5		
HMX				
P	5	5279.2	10.67	0.001*
Within cell error	18	494.9		
DNT				
P	5	165.1	<1	NS
Within cell error	18	333.5		

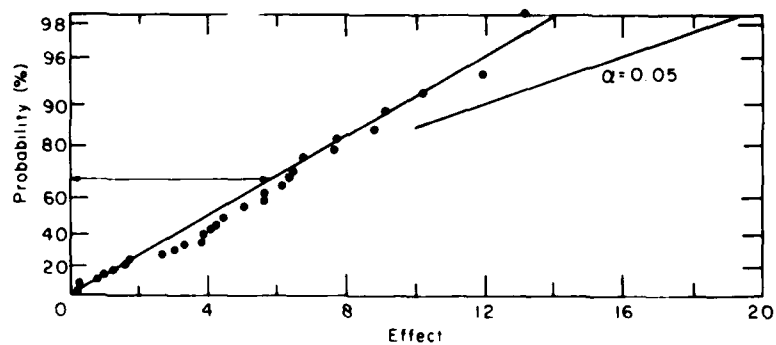
\*Highly significant.



a. TNT.

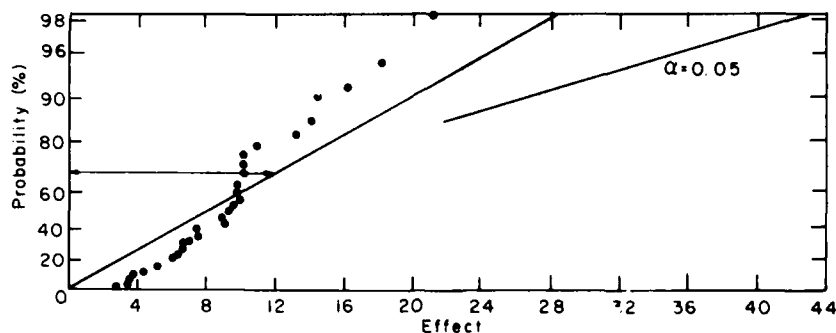


b. RDX.



c. HMX.

Figure A1. Cuthbert Daniel plots for experiment I.



d. DNT.

Figure A1 (cont'd).

Table A3. Results of least significant difference test on data from experiment I, day 80.

TNT  
LSD<sub>0.05</sub> = 63

511a   464b   441e   427f   412d   398c

RDX  
LSD<sub>0.05</sub> = 23

2062b   2026f   2011a   2005d   2004c   2003e

HMX  
LSD<sub>0.05</sub> = 33

348e   346a   335b   309c   288d   256f

- a Glass control
- b Esilon 2-in. schedule 40 pipe
- c Timco 2-in. schedule 40 pipe
- d Timco 2-in. schedule 40 well screen
- e Timco 2-in. schedule 80 pipe
- f Timco 4-in. schedule 80 pipe



Table A4. Analysis of variance of the  
four explosives, experiment II, day 25.

Term*	DF	Mean square	F	Level of significance
TNT				
S	1	406.1	<1	NS
P	1	5304.5	7.50	0.025
SP	1	903.1	1.28	NS
D	1	2080.1	2.94	NS
SD	1	1058.0	1.50	NS
PD	1	10878.1	15.37	0.001*
O	1	9870.1	13.97	0.001*
SO	1	84.5	<1	NS
PO	1	561.1	<1	NS
OD	1	5832.0	8.24	0.025
G	1	4704.5	6.65	0.025
SG	1	435.1	<1	NS
PG	1	338.0	<1	NS
DG	1	3916.1	5.53	0.050
OG	1	36.1	<1	NS
Error	16	707.6		
RDX				
S	1	1200.5	1.02	NS
P	1	882.0	<1	NS
SP	1	3570.1	3.04	NS
D	1	7938.0	6.76	0.025
SD	1	136.1	<1	NS
PD	1	6.1	<1	NS
O	1	24753.1	21.06	0.005*
SO	1	684.5	<1	NS
PO	1	3612.5	3.07	NS
OD	1	882.0	<1	NS
G	1	4095.1	3.48	NS
SG	1	3612.5	3.07	NS
PG	1	924.5	<1	NS
DG	1	4512.5	3.84	NS
OG	1	0.1	<1	NS
Error	16	1175.1		

S = presence or absence of  $MgCl_2$  and  $CaCl_2$  salts.

P = pH, pH = 6 or 8.

D = microbial degradation - presence or absence of bactericidal agent.

O = dissolved oxygen, high or low.

G = glass vs PVC.

\* = highly significant.

Table A4 (cont'd).

Term*	DF	Mean square	F	Level of significance
HMX				
S	1	331.5	1.06	NS
P	1	247.5	<1	NS
SP	1	157.5	<1	NS
D	1	830.3	2.65	NS
SD	1	57.8	<1	NS
PD	1	657.0	2.10	NS
O	1	81.3	<1	NS
SO	1	116.3	<1	NS
PO	1	247.5	<1	NS
OD	1	357.8	1.14	NS
G	1	87.8	<1	NS
SG	1	140.3	<1	NS
PG	1	22.8	<1	NS
DG	1	294.0	<1	NS
OG	1	116.0	<1	NS
Error	16	313.5		
DNT				
S	1	371.3	<1	NS
P	1	2032.0	2.94	NS
SP	1	148.8	<1	NS
D	1	2682.8	3.88	NS
SD	1	1365.0	1.97	NS
PD	1	457.5	<1	NS
O	1	1554.0	2.25	NS
SO	1	1696.5	2.45	NS
PO	1	657.0	<1	NS
OD	1	770.3	1.11	NS
G	1	830.3	1.20	NS
SG	1	712.5	1.03	NS
PG	1	306.3	<1	NS
DG	1	108.8	<1	NS
OG	1	935.3	1.35	NS
Error	16	691.4		

S = presence or absence of  $MgCl_2$  and  $CaCl_2$  salts.

P = pH, pH = 6 or 8.

D = microbial degradation - presence or absence of bactericidal agent.

O = dissolved oxygen, high or low.

G = glass vs PVC.

**END**

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**11-85**

**DTIC**